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THE ODDA PROCESS AND ITS APPLICATION
IN LESS DEVELOPED AREAS

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The Odda Process and its Application in Less Developed Areas.

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1. Introduction

The fertilizer industry will be in a key position when modern agriculture and industry are going to be built up in less developed areas. It is not obvious though, that the structure of this industry in the old countries is adequate.

The new countries which in comparatively few years have to increase their production, must examine very carefully which processes to select for development of new fertilizer industry.

The production of ammonia and the supply of rock phosphate are two fundamental constituents for the fertilizer industry. To build a sulphuric acid plant especially for fertilizer production is no longer a necessity.

The production of concentrated complex fertilizers based on nitric acid may often be a preferable alternative. By treatment of rock-phosphate with nitric acid one obtains valuable calcium nitrate as a by-product instead of calcium sulphate from the sulphuric acid process.

The best existing fertilizer process based on the raw materials rock phosphate, nitric acid and ammonia is the Odda-process. Its main product is a nitrogen-phosphorus fertilizer usually with 20 % N and 9 % P., but the N/P ratio may be varied within wide limits. During the final granulation process other plant nutrients may be added in wanted amounts. A by-product of the process is calcium-nitrate, normally converted to prilled nitrate of lime with 15.5 % N.

The Odda process was invented by Erling B. Johnson, Odda, Norway, in 1928 and originally patented in Norwegian p. nr. 48644, and later in other countries, as British p. nr. 339340, French p. nr. 682423 and German p. nr. 573284. Several additional patents are also issued.

The process is used in Germany, Norway, Holland, France and Finland. Between 1.5 and 2.0 million tonnes complex fertilizer were produced last year by this process. - The production capacity is being increased. In Norway more than half the total fertilizer production, in Germany about a quarter and in Holland and France between 10 and 20 percent is made by the Odda process. - The different firms using the process have gained a considerable amount of experience, and technical problems arising during production have been overcome. The problems to be solved will be limited to local adaptability.

2. Description of the Odda Process

It is outside the scope of this paper to deal with the production of ammonia and nitric acid. It will here be assumed that these products are available from separate plants. It is also assumed that there is access to phosphate rock and other raw materials. Electric energy and cooling water must also be available at the site.

In figure 1. a flow sheet is given for the production of fertilizer by the Odda process. The main steps are as follows: - Phosphate rock is digested in nitric acid and the produced calcium nitrate tetrahydrate is crystallized out by cooling of the digested phosphate solution. The crystals are removed, melted, neutralised with ammonia and the water content reduced by evaporation. Finally nitrate of lime is prilled, cooled and screened. After the removal of the tetrahydrate crystals, the mother liquor is neutralised with ammonia, concentrated by evaporation, granulated - possibly with addition of potassium salts and other plant nutrients -, dried, cooled and screened.

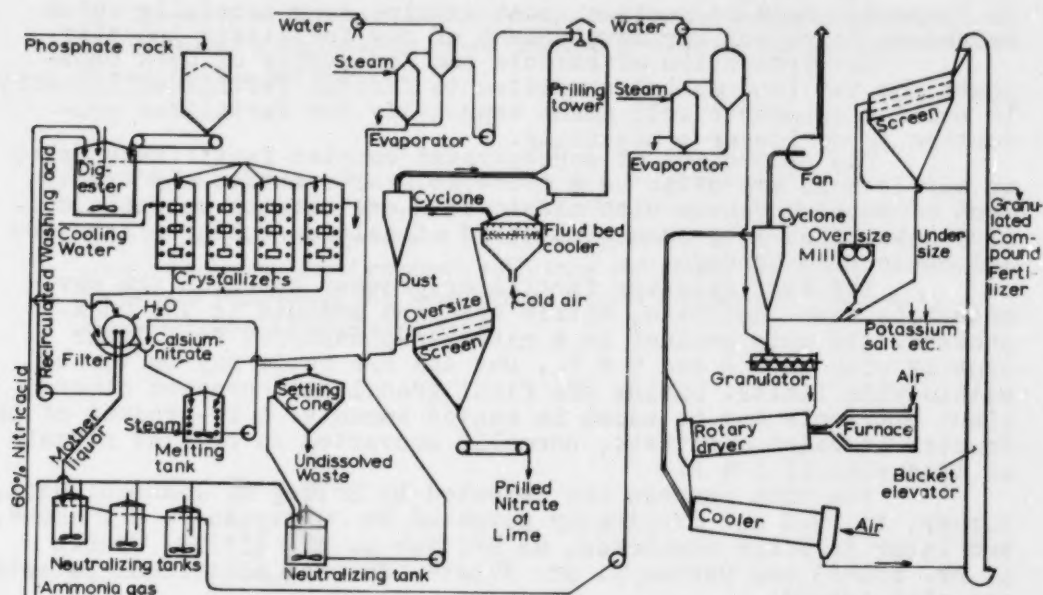


Fig. 1. Production of Granulated Compound Fertilizer and Prilled Nitrate of Lime by the Odda Process.

2 a. Raw Materials

Fundamentally any phosphate rock based on fluorine or hydroxy-apatite may be used. Chlorine-apatite will lead to

prohibitive corrosion problems. For favourable accomplishment of the process some limiting factors should be taken into account.

To obtain effective digestion 90 - 95 % of the ground phosphate should be less than 0.5 millimetres in diameter. Afterwards it should be dry enough for easy mechanical handling. Acid insoluble constituents ought not be more than two percent. A higher content is not prohibitive, but should preferably be separated from the digested liquor. Of acid soluble constituents, the highest possible content of calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, is desirable, preferably not less than 75 %. The best available phosphate rocks contain about 85 %. A certain amount of CaCO_3 is by itself not harmful, but it will increase the amount of calcium nitrate to be removed. Iron compounds may cause a reduction of citrate soluble phosphorus in the final product and should preferably not exceed 0.7 - 0.9 %, - calculated as iron. Organic matter may act as foam stabilizers and lead to troublesome foaming. The problem may be overcome either with antifoaming agents or by mechanical foam killing devices.

In general all commercial phosphate rocks on the world market can be used for the process. It should also be possible to adapt the process to more special types if necessary.

The nitric acid should be in the concentration range 58 - 61 %. Ammonia may be used either in the liquid or the gas phase. Ammonia mixed with inert gases may also be used.

2 b. Digestion of Phosphate Rock with Nitric Acid

Ground phosphate rock and nitric acid are continuously proportioned in a mixer tank fitted with overflow. In some cases the necessary digestion time makes it desirable to divide the system into several mixing tanks in series.

The proportion of acid to phosphate depends to a certain degree on the type of phosphate used. An excess of at least 15 %, preferably 20 - 25 % of the calculated amount of acid should be used to obtain favourable working conditions. For common types of phosphate rocks 1.3 - 1.5 parts of HNO_3 to 1.0 part of phosphate rock, weight/weight, gives the right ratio.

The exothermic dissolution process yields about 70 M cal per tonne dissolved phosphate rock. The temperature rise is 45°C . In normal conditions the temperature of the digested solution is between $55 - 70^\circ\text{C}$. The solution consists of a mixture of nitric, phosphoric and a little hydrofluoric acid, as well as dissolved calcium nitrate with different other dissolved and undissolved impurities.

2 c. Crystallization of Calcium Nitrate.

The saturation point of calcium nitrate is obtained in the temperature interval $25 - 28^\circ\text{C}$ when the warm phosphate solution is cooled. By continued cooling $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ is crystallized out. This is the key point of the Odda process. Crystallization is used for removal of excess, undesired calcium from the phosphate solution. In figure 2 the Ca/P ratio of the mother liquor is plotted

versus the temperature. The graph indicates the amount of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystallized out.

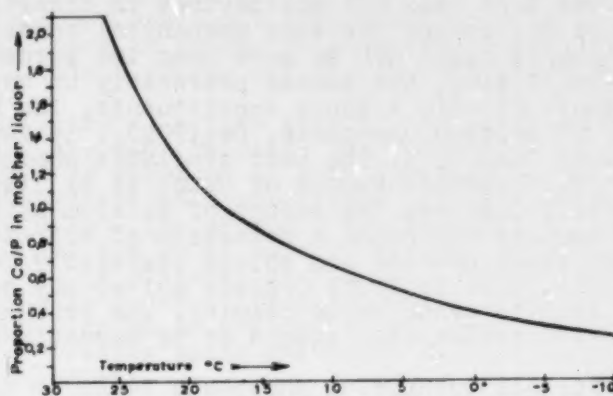


Fig. 2. Crystallization of $\text{Ca}(\text{NO}_3)_2$ from digested phosphatic liquor of the composition given in the later material balance example.

The cooling process is normally carried out in vessels equipped with stirring and coils cooled by water or circulating brine. The process can be carried out continuously or batchwise. Both systems are used and each have their particular advantages and disadvantages. Continuous crystallization has the advantage of uniform flow which is suitable for the rest of the process. The crystallizers however, have to be shut down at few hours intervals to remove salt deposits from the cooling surface. The method also gives crystals of varied size, and mixed with the undissolved impurities the resulting salt cake will be rather compact making the passage of mother liquor difficult. Effective centrifuges are necessary for the removal of mother liquor from the solid matter.

The batch process has the disadvantage of interrupted flow and requires buffer volume. - In this case though, the regeneration of the cooling surface is a natural part of the batch cycle when filling the crystallizer with warm solution. By seeding at a predetermined supersaturation point it is possible to control the number and the size of the crystals. Very uniform particle size is produced by this method. The crystals form a cake with large open area making the drainage of mother liquor easy. It can be done on a stainless steel mesh filter with a mesh size about 0.5 mm. Small undissolved particles will pass through the cake and filter medium and accompany the mother liquor after filtration.

2 d. Separation of Calcium Nitrate Crystals and Conversion to prilled Nitrate of Lime.

As previously mentioned the separation of the crystals from the mother liquor depends on the crystallisation method used. For continuous crystallization preferably two centrifuges in series

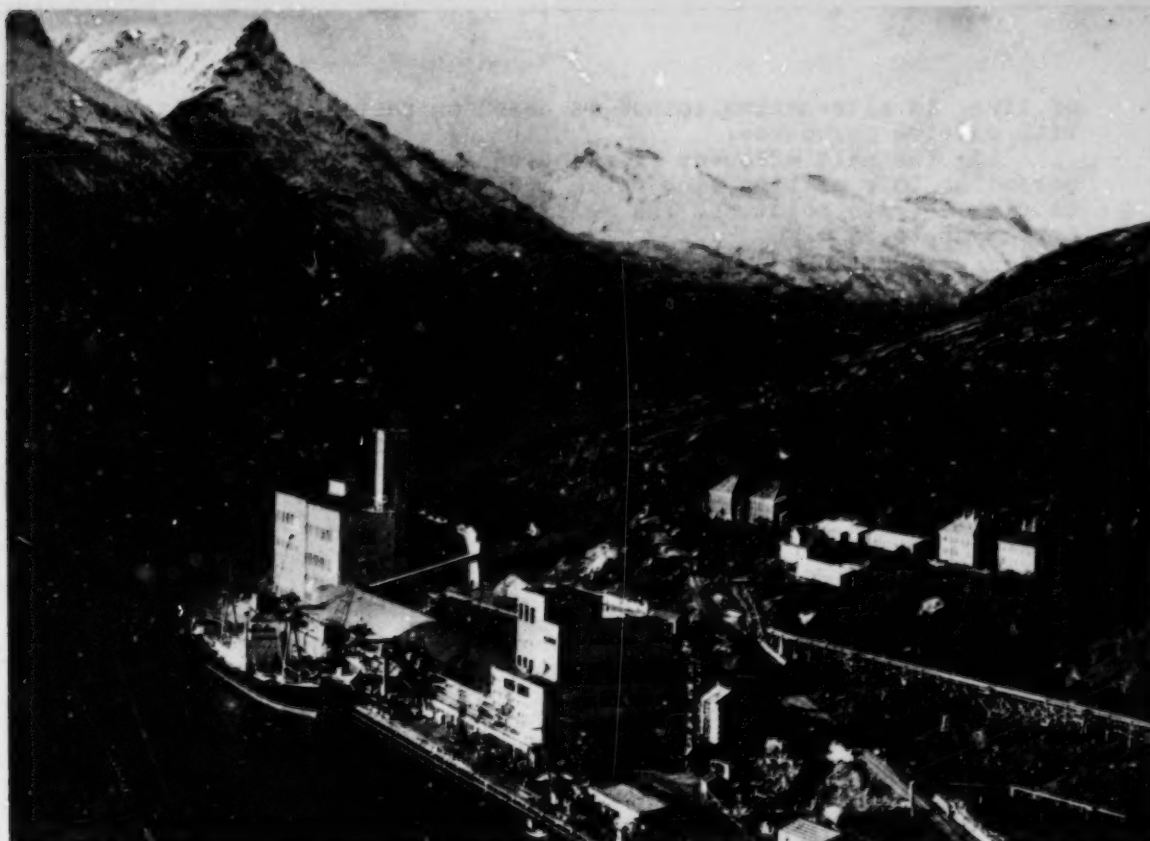


Figure 3.

The Norsk Hydro NPK plant situated 30 kilometres north of the Polar circle at Glomfjord, Norway. About 300 000 tonnes of complex fertilizer is made by the Odda process pro annum.

are used with an intermediate wash of the crystals in nitric acid. The mixture of nitric acid and mother liquor is returned to the digestion stage.

With batch-crystallization the separation is easier. A continuous vacuum filter with a filter mesh as previously described may be used. The nitric acid wash is carried out on the same filter unit. The capacity is about two tons of dry weight cake per hour per square metre filter area. Washing will reduce the mother liquor content to less than 2 % of cake weight. Some of the nitric acid in the cake may be displaced by water before discharge. In this way it is possible to regulate the ammonium nitrate content in the nitrate

of lime. An alternative method is based on partial neutralization with calcium carbonate.

The salt effluent from the centrifuge or the filter is passed on to a melting tank using a circulating stream of hot calcium nitrate solution. The melting point of calcium nitrate tetrahydrate is 42°C.

The acidic calcium nitrate solution is usually clarified by means of a settling cone, and thereafter neutralized by ammonia gas. The neutral solution is concentrated by evaporation and pumped through spray nozzles into a prilling tower. Here the drops are solidified when falling countercurrently to air with an inlet temperature of 10°C and outlet temperature of about 50°C. The prills from the tower which possess a temperature of about 60°C, are further cooled to room temperature by cold air, preferably in a fluid bed and finally screened. Dust and oversize material is recycled to the melting tank, and the final product of the calcium nitrate stream, prilled nitrate of lime, is ready for storage or packing.

2 e. Neutralization of the Mother Liquor.

The mother liquor from the calcium nitrate separation is passed on to the neutralization stage after adjusting the composition, if necessary, by adding nitric acid and/or phosphate rock.

Neutralization is from a chemical point of view the most complicated step of the process. In spite of considerable research, knowledge of reaction mechanisms and side-reactions is rather limited. The methods and apparatus for carrying out the neutralization are for this reason based mainly upon experience.

The main constituents of the mother liquor are HNO_3 , H_3PO_4 , HF , H_2SiF_6 , $\text{Ca}(\text{NO}_3)_2$ and H_2O . The main reactions taking place when ammonia is added and the pH raised from 0.5 to 5.5 are the following:

1. $\text{NH}_3 + \text{HNO}_3 = \text{NH}_4\text{NO}_3$
2. $2\text{NH}_3 + 2\text{HF} + \text{Ca}(\text{NO}_3)_2 = \text{CaF}_2 + 2 \text{NH}_4\text{NO}_3$
3. $2\text{NH}_3 + \text{H}_2\text{SiF}_6 + \text{Ca}(\text{NO}_3)_2 = \text{CaSiF}_6 + 2 \text{NH}_4\text{NO}_3$
4. $\text{NH}_3 + \text{H}_3\text{PO}_4 = \text{NH}_4\text{H}_2\text{PO}_4$
5. $\text{NH}_3 + \text{NH}_4\text{H}_2\text{PO}_4 = (\text{NH}_4)_2\text{HPO}_4$
6. $(\text{NH}_4)_2\text{HPO}_4 + \text{Ca}(\text{NO}_3)_2 = \text{CaHPO}_4 + 2\text{NH}_4\text{NO}_3$

Reactions 1, 2 and 3 take place in the pH range 0.5 - 2.5 and the others above pH 2. The main constituents of the neutralized slurry are solid CaHPO_4 , CaF_2 , CaSiF_6 and dissolved NH_4NO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$. The proportion of calcium phosphate to ammonium phosphate will depend upon the Ca/P ratio in the mother liquor. In this way it is possible to regulate the content of water

soluble phosphorus by the removal of calcium nitrate in the crystallization stage.

In addition to the desired main reactions, many others take place. Ammonium calcium phosphate may be formed, and the product may thus contain some (f.ex. 0.5 %) water insoluble nitrogen. Iron content will initiate side-reactions which disturb the phosphate precipitation. Citrate soluble FePO_4 as well as more complex citrate insoluble iron phosphates may be formed. Aluminium does not seem to form similar reaction products. Under unfavorable conditions reoccurrence of fluorine or hydroxy-spatite may be observed, but this may be avoided by performing the neutralization in several steps.

The heat of neutralization is about 1250 M. cal per tonne NH_3 and will raise the temperature to the boiling point, with considerable evaporation taking place. The viscosity will normally be comparatively low, and the neutralized slurry will easily flow through an evaporator. In certain cases the liquor will have marked thixotropic character, and may become pasty.

Different explanations are given to explain the colloidal conditions which depend on the types of phosphate rock used. The phenomenon is, however, not clearly understood. In specific cases experiments are necessary for the evaluation of rock phosphate to be processed.

Neutralization is normally carried out continuously by flow through two to four successive vessels equipped with stirring, where the ammonia is put into the liquor. The pH is raised from 1.5 to 3.5 in the first step and to about 5.5 to 6.0 in the last.

The evolution of steam may take place in the reaction vessels. The liquor can also be circulated through separate vacuum evaporators. In the last case the ammonia absorption is better, but the apparatus is more complicated.

The neutralized slurry has a temperature of 115 - 130°C, about 10 - 15 % water and a specific gravity of 1.6. A further reduction of the water content is advantageous before granulation and is normally carried out in vertical tube evaporators at reduced or atmospheric pressure. A water content of about 5 % in the slurry is easily obtained with good flow properties in the temperature range 125 - 140°C.

2 f. Granulation and Drying.

No special modifications are needed for the granulation in the Odda process. Solidification on a water cooled rotary drum followed by drying, screening etc. has been used, but gives a rather flaked and edgy product. Cooling prior to drying is also bad from a heat economic point of view. Prilling in spray towers gives uniform, nice prills for certain qualities, especially for NP-fertilizers when larger amounts of additives (potassium and magnesium salts etc.) are used. The spraying itself, however, is more difficult, and the prilling procedure is not often used for this type of fertilizer.

The method most commonly in use is the following: - Measured quantities of NP-slurry are continuously mixed with weighed amounts of the dry raw materials (potassium and magnesium compounds etc.) in a double screw granulator. Recycled dust and ground oversize product is part of the feed-stock. Moist granules of variable size formed are passed into a direct rotary dryer, usually oilfired. In the first section of the rotary dryer, the granulation is

completed simultaneously with the preliminary drying. Some grinding action takes place to a certain degree in the final drying section and in the following countercurrent cooler. The cooled material is screened; undersize particles below 1.0 - 1.5 mm and oversize product above 3.5 - 4.5 mm is recycled to the granulator, the coarse fraction via a grinder. The exhaust air from the dryer and the cooler is passed through a dust separator and the dust returned to the granulator.

The granulator temperature is 70 - 90°C, outlet temperature from the dryer 90 - 100°C and discharge temperature from the cooler 40 - 80°C.

Exothermic decomposition starts if the material is heated above 200 - 250°C with evolution of nitrous and nitric oxide, nitrogen and ammonia. Nitrosylchloride and chlorine may also be present in the decomposition products. The velocity of the decomposition reaction is rather low, and if discovered on an early stage, reacting lumps can easily be removed. In a later phase the decomposition reaction can be distinguished with water. Because of the decomposition risk, the temperature of the flue gas entering the dryer should not exceed 250°C. For the same reason parallel flow is chosen.

The water content in the material after granulation is 2 - 4 % and in the dryer 0.2 - 1.0 %.

The granulation method normally yields 35 - 45 % product and 55 - 65 % recycled material. Total cycling time is about 50 minutes, of which 25 minutes in the dryer, 20 minutes in the cooler and 5 minutes for the rest.

During storage the fertilizer product may have a tendency for caking. To avoid this, the granulated product is usually powdered with kieselguhr or other suitable conditioning agents.

3. Feedstock, Energy, Investment and Staff Demands.

The production of NP-fertilizer with 20 % N, 9 % P and nitrate of lime with 15.5 % N is chosen in table 1 as a representative example. The raw materials are calcined Morocco-phosphate with 16.0 % P and 39.0 % Ca, 60 % nitric acid and ammonia gas.

Table 1

Material balance. Basis 1000 kg P:

	Total amount	NH ₃ -N	NO ₃ -N	P	Ca	H ₂ O
	kg	kg	kg	kg	kg	kg
<u>Digestion:</u>						
Phosphate rock:	6250	-	-	1000	2410	-
Nitric acid:	14600	-	1945	-	-	5850
Recycled mother liquor:	4000	-	307	312	332	1060
Digested liquor:	24850	-	2252	1312	2772	6910
<u>Crystallization and filtration:</u>						
Removed Ca(NO ₃) ₂ · 4H ₂ O:	8200	-	973	10	1390	2500
Recycled mother liquor:	4000	-	307	312	332	1060
Mother liquor:	12650	-	972	990	1050	3350
<u>Neutralization:</u>						
Ammonia gas:	1490	1230	-	-	-	-
Water evaporated by heat of reaction:	2150	-	-	-	-	2150
Neutralized NP-slurry:	11990	1230	972	990	1050	1200
<u>Evaporation and drying:</u>						
Water removed:	1150	-	-	-	-	1150
<u>NP-fertilizer:</u>	10840	1230	972	990	1030	50

Table 1 continued

	Total amount	NH ₃ -N	NO ₃ -N	P	Ca	H ₂ O
Production of nitrate of lime:	kg	kg	kg	kg	kg	kg
Removed Ca(NO ₃) ₂ · 4H ₂ O:	8200	-	973	10	1390	2500
Remaining water and acid in cake:	770	-	76	-	-	430
Ammonia for neutralization:	92	76	-	-	-	-
Water removed by evaporation:	1882	-	-	-	-	1882
Prilled nitrate of lime:	7180	76	1049	10	1390	1048

The production losses are not taken into account in this balance, but they amount to about 0.5 % of the NO₃-N, to 1.5 - 2.0 % of NH₃-N and 1 % of the phosphorus. The corresponding energy demands for the material balance amounts to:

840 M. calories for crystallization cooling equal to 50 m³ water inlet temperature 8°C, outlet temperature 25°C. For prilling and cooling the nitrate of lime 18 000 m³ air at + 10°C and 7000 m³ air at - 10°C are needed. For an outdoor air temperature of 35°C the energy demand equals 240 M. cal. Nitrogen originally present as liquid ammonia gives 1200 M. cal. of cooling, corresponding to a net excess of 120 M. cal. In addition about 170 m³ water preferably not warmer than 25°C is needed for condensers etc.

Steam demands are 3.2 ton s for melting, heating and evaporation of nitrate of lime, 0.6 ton s for evaporation of NP-slurry and 1.2 ton s for other purposes, a total of 5.0 ton s. The production of nitric acid from ammonia gives 8.7 tonnes of steam or an over all excess of 3.7 ton s available for other purposes.

The consumption of fuel oil for drying of the NP or NPK fertilizer is about 0.1 ton . The electric energy demand for mechanical power is about 0.7 MWh.

If one assumes that the above data for materials and energy correspond to one hour's production, then the annual production capacity is 85 000 tonnes NP-fertilizer, or f.ex. 130 000 tonnes NPK 13-6-17, - a plant of reasonable size.

The investment cost depends to some extent on local conditions, as a rough guide 2.5 - 3.0 million \$. A corresponding nitric acid plant amounts to 1.5 - 2.0 million \$. Costs for roads, quays, stores packing equipment etc. come in addition.

In charge of the work a plant superintendant and a plant manager are needed. The necessary additional staff for continuous shift work will be 6 process workers, 1 in the laboratory and 1 foreman. For day time work 4 - 5 general workers with a foreman, 2 - 3 chemists and 4 - 5 skilled maintenance workers with a qualified foreman should be sufficient. It is assumed that more specialized technical services are available outside the works.

4. The Adaptability of the Process to different Regions.

The Odda process as described above, may be applied anywhere in the world assuming the conditions are suitable for making fertilizer, or if desirable, may be modified to suit different demands.

The chemical composition may be varied to meet any agricultural requirement. The proportion of water soluble P to the total available amount, which is normally 1 : 3, may be increased to about 9 : 10 by further cooling in the crystallization stage. A higher concentration of plant nutrients is hereby obtained, corresponding to a maximum of f. ex. 24 % N and 10.5 % P.

The weight ratio N/P should not be lower than 1.8/1 for a normal Ca/P ratio. The content of N may be varied at convenience upwards. Other plant nutrients may be added to the NP-component.

The production of compound fertilizer may be combined with the production of ammonium phosphate or a mixture of ammonium-phosphate and ammoniumnitrate if a concentrated, entirely water soluble NP fertilizer is desired. (Norwegian p. nr. 86 066, British p. nr. 757 835, French p. nr. 1114 320 and German p. nr. 953 531).

As seen previously, the cooling demand is satisfied by evaporation of input ammonia, but if this cooling capacity should be desirable for other purposes and cooling water of maximum 15°C is available, the Hydro process may be preferable. In this case nitric acid of about 65 % is used and to some extent neutralized by ammonia prior to digestion. By cooling to 23°C sufficient calcium nitrate is removed as $\text{NH}_4\text{NO}_3 \cdot 5\text{Ca}(\text{NO}_3)_2 \cdot 10\text{H}_2\text{O}$. (Norwegian p. nr. 60 374, British p. nr. 391 328, French p. nr. 738 210, German p. nr. 650 344).

In tropic areas the rather hygroscopic nitrate of lime may be found less convenient. In that case it is possible to convert the calcium nitrate into ammonium nitrate limestone by means of NH_3 and CO_2 . Another and probably more suitable alternative for tropic areas is to make a nitrogen solution consisting of 34 % calcium nitrate and 32 % ammonium nitrate which has a nitrogen content of 17 % and a crystallization point of 4°C. When the pH of this solution is kept above 7, it can be stored and distributed in mild steel tanks. This application of the separated calcium nitrate will eliminate the nitrate of lime part of the plant, and thus reduce the necessary investment.

Also the NP or NPK fertilizer can be stored and transported in bulk and distributed in containers if that is found convenient.

From an agricultural point of view the NP or NPK fertilizer made by the Odda process with its wide possibilities for variation in composition, should be fit for all main purposes. Up to this time, however, the production and consumption of this fertilizer is mainly concentrated in the northern and the middle part of Europe.

As a rough guidance the fertilizing efficiency corresponds to the same amount of plant nutrients added as straight materials. In some one year field tests a few percent lower effect is found. than in the reference straight material test where superphosphate is used as the phosphorous compound. It is assumed that the lower effect is due to a slower action of the dicalcium phosphate in the compound fertilizer than of the monocalcium phosphate in the superphosphate.

The calcium phosphate not taken up by the plants, will build up a phosphorous surplus in the soil. In the long run it must be assumed that the difference will be negligible. The secondary elements may also be of appreciable importance in these comparative tests.

In more developed countries there is an increasing demand for concentrated ready - to - use fertilizers in order to save costs and labour. This demand will also be present in less developed areas, in any case after some years of development.

The danger for mistakes in the use of fertilizers will be least when the used material has a composition particularly suitable to local conditions.